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Estimating Emissions of Toxic Hydrocarbons from Natural Gas Production Sites in the Barnett Shale Region of Northern Texas

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Supporting Information

ABSTRACT: Oil and natural gas operations have continued to expand and move closer to densely populated areas, contributing to growing public concerns regarding exposure to hazardous air pollutants. During the Barnett Shale Coordinated Campaign in October, 2013, ground-based whole air samples collected downwind of oil and gas sites revealed enhancements in several potentially toxic volatile organic compounds (VOCs) when compared to background values. Molar emissions ratios relative to methane were determined for hexane, benzene, toluene, ethylbenzene, and xylene (BTEX compounds). Using methane leak rates measured from the Picarro mobile flux plane (MFP) system and a Barnett Shale regional methane emissions inventory, the rates of emission of these toxic gases were calculated. Benzene emissions ranged between 51 ± 4 and 60 ± 4 kg h^{-1}. Hexane, the most abundantly emitted pollutant, ranged from 642 ± 45 to 1070 ± 340 kg h^{-1}. While observed hydrocarbon enhancements fall below federal workplace standards, results may indicate a link between emissions from oil and natural gas operations and concerns about exposure to hazardous air pollutants. The larger public health risks associated with the production and distribution of natural gas are of particular importance and warrant further investigation, particularly as the use of natural gas increases in the United States and internationally.

INTRODUCTION

In recent years the development of energy from unconventional oil and natural gas (ONG) sources has grown substantially and has been hailed by some as an effective CO_2 mitigation strategy.[1] However, the fugitive emissions associated with the production and distribution of natural gas are atmospherically relevant and can potentially have large short-term climate impacts.[2−5] Methane (CH_4), the primary component of natural gas, has a global warming potential 86 times greater than CO_2 on a 20 year time scale and 34 times greater on a 100 year time scale.[6] In addition to the climatological impacts, ONG activities can have an effect on local air quality and potentially on human health. Increased CH_4 in the atmosphere can lead to the formation of surface ozone, meaning its impacts are felt on both regionally and on a global scale.[7] Throughout the past decade, advances in horizontal drilling and hydraulic fracturing have made extraction of natural gas from these tight shale formations viable. In some instances, shale gas operations are in close proximity to densely populated areas. This has led to growing public concerns and numerous studies regarding exposure to hazardous air pollutants (HAPs).[8] These HAPs include gases such as hexane, 1,3-butadiene, benzene, toluene, ethyltoluene, and isomers of xylene (BTEX compounds), some of which can lead to minor health effects with short-term exposure or can potentially be carcinogenic with prolonged exposure.[9−12] While results of these studies show varying implications of these emissions, some studies have suggested a link between increased health risks and proximity of residents to ONG extraction and processing sites.[13−15]

The Barnett Shale of northern Texas is one of the most developed and productive ONG reservoirs in the United States. The region, which covers 5,000 square miles, is home to over 30,000 active conventional oil and natural gas wells (Figure 1).[16] During peak production in 2012, nearly 6 billion cubic feet (Bcf) of natural gas were produced per day, while a maximum of 4,600 barrels (Mbbl) of oil were generated daily in 2013.[17] As of 2015, the region is still responsible for roughly six

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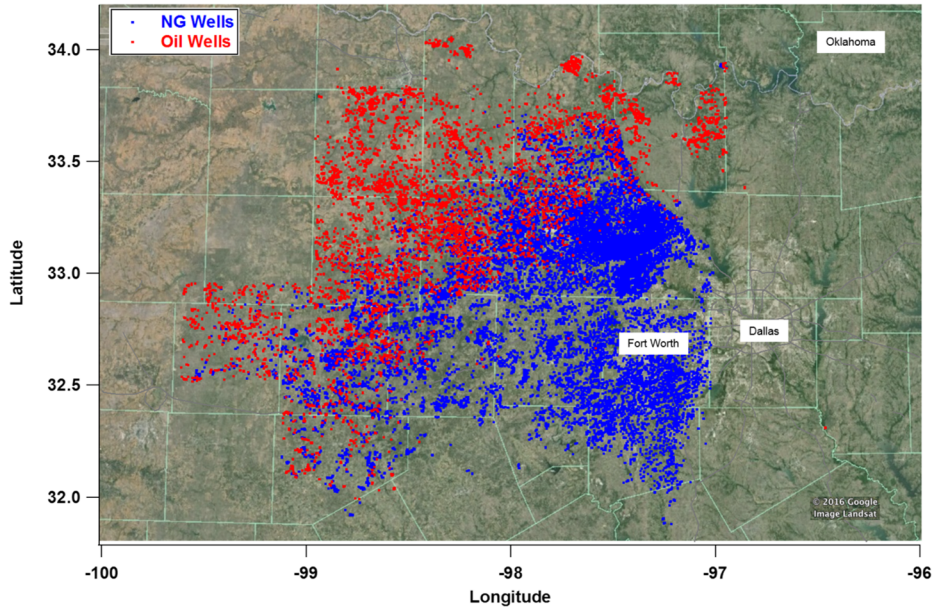

Figure 1. Map showing the location of oil and natural gas wells in the Barnett Shale region, with natural gas wells highlighted in blue and oil wells in red. Locations of the well sites obtained from Drillinginfo.[16]

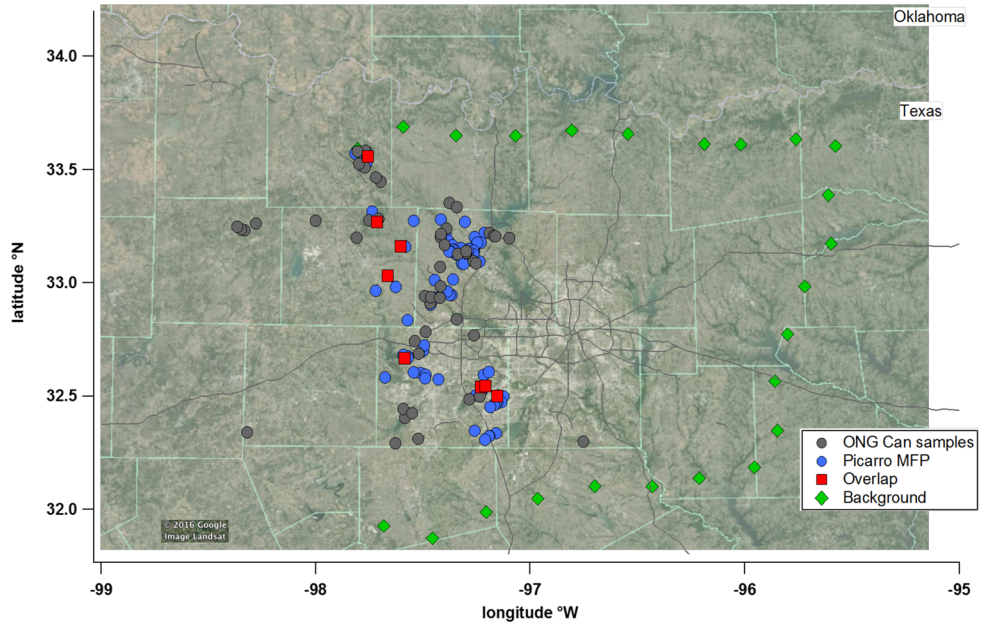

Figure 2. Map of the Barnett Shale region showing whole air canister sample locations (gray) and natural gas well pads sampled by the Picarro Mobile Flux Plane (blue). At 8 locations, the two measurements were collected concurrently (highlighted in red). Background canister sample sites are shown in green.

percent of the nation's natural gas.[18] In addition to its large ONG infrastructure, the Barnett Shale is situated within one of the most populated regions in the country. Nearly 3 million people live within the production area, with the cities of Fort Worth and Arlington also contained within the core natural gas producing counties (Denton, Johnson, Tarrant, Wise).[17,19] Similarly to other ONG fields in the US, the proximity of this large residential population to oil and gas operations has intensified concerns about the potential health impacts of exposure to VOCs emitted from these sources.[20] In addition, this area (including the 4 core counties) is also designated as a moderate nonattainment area for exceeding the 2008 National Ambient Air Quality Standard for 8-h ozone of 75 ppb.[21] With the current 8-h standard reduced to 70 ppb, it is possible that exceedances may become more common in the region.

The natural gas industry now serves as the largest anthropogenic source of CH_4 nationally[22] and has long been regarded as a source of hydrocarbon pollution.[23] Consequently, recent studies have focused on more accurate quantification of CH_4 emissions from the natural gas industry in various shale plays across the United States.[24−27] However, accurate quantification has proven difficult, with studies varying widely in CH_4 estimates and large discrepancies occurring between top-down and bottom-up approaches.[28,29] The Barnett Coordinated Campaign was conducted from October 16−30, 2013, and consisted of multiscale measurements to quantify

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Table 1. Average Mixing Ratios Observed in Well Mixed Air and Downwind of Oil and Natural Gas Sources in the Barnett Shale[a]

	CH_4 (ppmv)	hexane (C_6H_{14})	benzene (C_6H_6)	toluene (C_7H_8)	ethylbenzene (C_8H_{10})	*m*/*p*-xylene (C_8H_{10})	*o*-xylene (C_8H_{10})
background (n = 24)	1.95 (0.07)	200 (140)	100 (44)	150 (110)	20 (15)	66 (44)	22 (18)
oil wells (n = 12)	4.33 (4.27)	9710 (18300)	820 (1300)	2310 (5270)	140 (240)	2600 (7770)	310 (760)
NG wells (n = 31)	4.35 (5.87)	3210 (9400)	290 (500)	590 (1190)	56 (130)	510 (1460)	86 (200)
dry gas (n = 17)	6.36 (7.20)	860 (1310)	230 (320)	360 (430)	50 (75)	200 (280)	60 (80)
wet gas (n = 35)	4.60 (5.55)	6780 (13700)	590 (940)	1360 (3170)	100 (180)	1360 (4520)	180 (470)
compressor stations (n = 10)	8.12 (7.85)	3700 (5840)	610 (800)	910 (1080)	100 (130)	550 (730)	120 (100)
distribution and storage (n = 5)	3.89 (0.51)	530 (410)	170 (10)	230 (90)	50 (49)	180 (240)	50 (60)
gathering and processing (n = 3)	2.43 (0.45)	590 (240)	130 (70)	270 (120)	25 (8)	90 (30)	34 (10)
fracking wells (n = 2)	2.10 (0.05)	690 (100)	190 (90)	770 (680)	55 (25)	150 (80)	51 (40)

[a]Wet and dry gas wells were distinguished based on $\%C_2H_6$. 1σ standard deviation shown in parentheses. Units for all compounds are in pptv unless otherwise noted.

CH_4 emissions from the various sources in the region, including whole air sampling.[30] Unlike hydrocarbon measurements at regional monitoring locations, whole air samples were collected downwind of individual ONG sites, providing a snapshot of emissions. Our previous work using the same samples paired alkane and stable isotope ratios of CH_4 sources in the region with a bottom-up inventory to aid in comparison to top-down CH_4 estimates.[31] Presented here are measurements and emissions estimates of *n*-hexane and the BTEX compounds for the greater Barnett Shale region, utilizing the VOC to CH_4 ratios determined from whole air samples combined with mobile flux measurements and a bottom-up CH_4 emissions inventory.

METHODS

Whole Air Samples. During October 2013, whole air samples were collected downwind of various thermogenic CH_4 sources throughout the Barnett Shale (one sample at each location). Oil and natural gas (ONG) sample locations included natural gas well pads (n = 31), some of which housed separators, condensate tanks, or compressors in addition to the well heads; conventional oil wells (n = 12); compressor stations (n = 10); distribution city gates (where gas is held before delivery to consumers) and storage facilities (n = 5); and gathering and processing facilities (n = 3). In addition, "background" samples representative of well mixed air in the Barnett shale, both up and downwind, were collected away from point sources. Sample locations, primarily focused on the western edge of the Barnett Shale, are shown in Figure 2. Sample collection was guided by a Picarro Instruments G2301, powered by a vehicle alternator, which analyzed CH_4, CO_2, and H_2O. Downwind of point sources, the GHG analyzer was used to detect enhancements in CH_4 of at least 50 ppb over typical ambient CH_4 concentrations on that day, with the instrument inlet located upwind of the vehicle. Conversely, on the day in which regional background samples were collected, the analyzer was used to ensure that no enhancements in ambient CH_4 were observed before a canister was filled.

Whole air samples were collected in 2 L electropolished stainless steel canisters, evacuated to a pressure of 10^{-2} Torr. Canisters were preconditioned before sampling, by baking at 150 °C and flushing with ultrahigh purity helium. Air samples were then returned to the University of California, Irvine for analysis on a multicolumn, multidetector gas chromatographic system, described in detail elsewhere.[32] Trace gases measured include CO, CO_2, CH_4, and other C_2-C_{10} hydrocarbons (alkanes, alkenes, aromatics), of which only unbranched alkanes and BTEX compounds were utilized in subsequent calculations. The limit of detection for hydrocarbons is 3 parts per trillion (pptv), with analytical precision and accuracy of 3% and 5%, respectively. VOCs are calibrated to NIST traceable absolute hydrocarbon standards or in-house standards that have undergone extensive intercomparison.[33,34]

Methane Flux Measurements. Methane emissions from well pads were quantified utilizing the Mobile Flux Plane (MFP) method, as described by Rella et al.[35] Briefly, a vehicle outfitted with a GPS, anemometer, and CH_4 analyzer is driven on the downwind side of a well pad. Ambient CH_4 is measured through a series of vertical inlets from the base of the vehicle to a height of approximately 4 m above ground. Sample reanalysis of CH_4 is triggered upon detection of a plume and along with position and vertical wind speed, the emission rate is calculated (kg h^{-1}). At an average distance of 34 m, the detection limit is 0.034 kg h^{-1} and measurement accuracy is 24%.[35] At some ONG well pads (n = 8), MFP measurements and whole air samples were collected concurrently (Figure 2), allowing for a full hydrocarbon profile to be obtained along with CH_4 fluxes.

Methane Emissions Inventory. Regional emissions from the various CH_4 sources in the Barnett Shale were estimated through a spatially resolved inventory developed by Lyon et al.[29] In summary, experimental data collected at ONG sites throughout the area were used along with national data on gathering and processing facilities to categorize the sources. Emission factors accounting for the fat-tail distribution (few sites with large emissions) were then calculated and used to determine overall CH_4 inventory estimates.[29] The inventory estimated that approximately two-thirds of total CH_4 emissions are from thermogenic (ONG) sources.

RESULTS AND DISCUSSION

Ambient Mixing Ratios and Hydrocarbon Composition. Average mixing ratios of CH_4 and select hydrocarbons determined from whole air samples of background air and downwind of ONG wells are summarized in Table 1. An in-depth characterization of the light alkanes associated with thermogenic CH_4 sources is presented in Townsend-Small et al.,[31] and the primary focus of the current study is the toxic VOCs. For each of the ONG sources sampled in this study, VOCs were enhanced from 2 to nearly 50 times over background (Table 1). For similar CH_4 values, conventional oil wells generally showed higher concentrations than natural gas well pads for each of the hazardous air pollutants,

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Table 2. Hydrocarbon Composition As Described by Average Percentage of Alkane and Aromatic Compounds Present in All Source Types Sampled in the Barnett Shale[a]

	CH_4 (%vol)	C_2H_6 (%vol)	C_3–C_5 (%vol)	n-C_6H_{14} (%vol)	BTEX (%vol)	BTEX (%mass)
conventional oil	77.5 (7.0)	9.7 (2.2)	12.3 (2.8)	0.4 (0.2)	0.2 (0.2)	0.79
natural gas wells	87.6 (11.0)	6.5 (4.7)	5.7 (4.5)	0.2 (0.1)	0.1 (0.1)	0.38
compressor stations	87.8 (16.8)	5.2 (3.1)	6.7 (5.8)	0.2 (0.3)	0.1 (0.1)	0.42
gathering and processing	93.8 (4.9)	3.5 (2.1)	2.6 (1.3)	0.1 (0.1)	<0.1	0.15
distribution and storage	95.9 (1.5)	3.3 (1.5)	0.8 (0.5)	<0.1	<0.1	0.08
dry ONG					<0.1	0.29
wet ONG					0.1 (0.1)	0.58
ERG ONG[37]						1.36

[a]For butane and pentane, both the iso- and n-isomers were included in calculations (for a total of 13 compounds).

Table 3. Methane Fluxes Measured by the MFP System and Corresponding Mixing Ratios from Canister Samples Filled Concurrently[a]

MFP CH_4 flux (kg/h)	CH_4 (ppmv)	C_6H_{14} hexane	C_6H_6 'B'	C_7H_8 'T'	C_8H_{10} 'E'	C_8H_{10} m/p-'X'	C_8H_{10} o-'X'
0.26	5.008	91	80	81	10	31	13
0.82	2.437	5425	465	450	54	180	51
2.92	2.040	410	160	220	16	86	20
3.71	2.937	340	240	1080	78	300	140
3.77	5.033	110	73	110	26	94	30
4.97	3.719	6850	510	730	45	610	93
6.94	16.94	55900	3470	17710	800	26000	2580
13.78	15.23	52330	2745	6145	650	6970	1210

[a]CH_4 is reported in ppmv, while the remaining gases are in pptv.

particularly hexane, which was elevated over background by a factor of 48. Measurements taken downwind of natural gas processing facilities showed some of the lowest VOC mixing ratios of the ONG sources, reflecting the removal of higher chained hydrocarbons before the natural gas is distributed to consumers for use. Interestingly, the distribution and storage samples, collected from pipelines, city gates, and a storage facility, did not have the lowest mixing ratios of hydrocarbons listed in Table 1. However, this could be due to conditions at those locations on the sampling date (wind direction, colocation of sources) and not because of increased hexane and BTEX content of natural gas from these sources (Table 2). Natural gas produced in the Barnett Shale is generally "dry", and the composition of distribution and storage samples represents an average of produced gas sources.

Standard deviations (1σ) are also listed in Table 1 and reflect the large variability among well pads from site to site. For reference, minimum, maximum, and median hydrocarbon values for each of the sources are listed in Table S1. The variability is partially due to the geographical and geological makeup of the Barnett Shale, which naturally separates out into regions of drier natural gas (highest CH_4 content), wetter gas (lower CH_4 content), and conventional oil. While not an absolute trend, analysis of the percent composition of light alkanes (C_2H_6 and C_3H_8) illustrated the relationship between geographic location and gas wetness (Figure 5 in Townsend-Small et al.).[31] The highest $\%C_3H_8$ values were found in samples collected in the oil-prone, northwestern portion of the Barnett Shale, while lower percentages were observed at natural gas well pads to the south and east.[31]

Utilizing the percent composition of alkanes, a distinction was made between wet and dry natural gas (Table 1). Samples that contained less than 5% C_2H_6 were classified as "dry", and those with more than 5% C_2H_6 were considered "wet", based on a typical range of C_2H_6 in natural gas of 2–11%.[36] When compared to dry natural gas, wet gas samples exhibited higher average mixing ratios (by a factor of 2–15) for nearly every VOC measured in this study, including the BTEX compounds. Further, in samples collected downwind of well pads producing wet gas, the BTEX content was 2 times greater than dry gas wells (Table 2). A report compiled by the Eastern Research Group (ERG) analyzed VOC content in emissions from oil and condensate storage tanks at 19 different well pads. The average BTEX percentage by mass in the ERG report was 1.36%.[37] By comparison, UCI oil and natural gas samples were 0.29–0.79% BTEX by mass. One possible explanation for this large difference is that condensate storage tanks hold natural gas liquids and often send dry natural gas to other locations, whereas the well pads where canister samples were collected did not all have storage tanks on-site. Another cause for this difference is sampling location – ERG measurements were taken directly at storage tanks and were not affected by atmospheric dilution like the canister samples in this study.

Hydrocarbon composition for each of the ONG sources sampled in this study is summarized in Table 2 (fractions normalized to 13 compounds listed, not total VOCs). Emissions from conventional oil wells were only 77.5 ± 7.0% CH_4 by volume, compared to 87.6 ± 11.0% for natural gas wells, and over 90% in processed natural gas. Likewise, hexane and BTEX composition are highest in oil wells and decrease throughout the natural gas supply chain. Despite higher average mixing ratios when compared to gathering and processing samples (Table 1), distribution gas is indeed the highest quality natural gas (95.9 ± 1.5% CH_4 by volume), containing the lowest levels of alkanes, hexane, or BTEX.

Emissions Estimates of Hazardous Air Pollutants. Methane flux measurements and VOC mixing ratios are listed in Table 3 for the 8 well pads where the MFP captured a plume and canisters samples were collected concurrently (Figure 2). The fluxes ranged from 0.26 kg h^{-1} to 13.8 kg h^{-1}, with the

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largest CH_4 flux values corresponding to the highest ambient mixing ratios of the hydrocarbons measured. The high mixing ratios were observed at wet gas wells (>5% C_2H_6) that also housed compressors and separators, used to separate raw natural gas from condensate (hydrocarbon liquids and water). These results are consistent with helicopter-based infrared camera surveys of ONG wells conducted in various US shale plays.[38] In the Barnett, 21% of well pads with the lowest gas-to-oil ratios (GOR) showed detectable emissions, compared to less than 1% of sites with higher GORs.

Utilizing the VOC to CH_4 ratio and the MFP flux measurements, C_6H_6 emissions, for example, were estimated for the Barnett Shale according to the following equation

$$C_6H_6 \text{ flux} = CH_4 \text{ flux (kg h}^{-1}) * (\text{MW } C_6H_6/\text{MW } CH_4) * (C_6H_6{:}CH_4)$$

where C_6H_6:CH_4 is given by the least-squares linear regression fit of the two gases. As seen in Figure 3, for these 8 canister

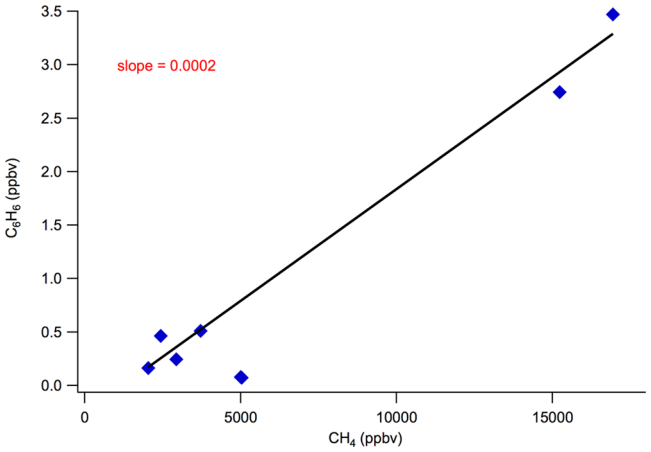

Figure 3. Molar ratio (slope) of C_6H_6 to CH_4 in whole air samples collected concurrently with Picarro MFP flux measurements (n = 8) throughout the Barnett Shale.

samples the molar ratio was $0.0002 \pm 2 \times 10^{-5}$, leading to an average benzene flux of 4.9 ± 1.5 g h^{-1}. Because this value is representative of emissions from an individual well pad, it was then scaled up for the region by the number of actively producing well pads (n = 17,000).[17] Using this method, the overall benzene emission estimate for the Barnett Shale is 84 ± 26 kg h^{-1}. However, this value assumes all well pads in the region have a detectable CH_4 leak rate and is therefore an overestimate of C_6H_6 emissions. Adjusting for the 63% of well pads believed to be leaking in Rella et al.[35] gives an average value of 53 ± 17 kg h^{-1} for the region. The same procedure was carried out for the remaining hazardous compounds of interest. Values are listed in Table 4, all in units of kg h^{-1}. Hexane was by far the most emitted HAP in the Barnett Shale, larger than the BTEX compounds by 1 to 2 orders of magnitude. It should be noted that emissions estimates are affected by the proportion of larger leaks that are sampled. The top 22% of emitters were found to be responsible for nearly 80% of overall well pad emissions.[35] Because canister samples were collected only when sizable leaks were detected, the calculated HAP emissions may be overestimated.

In a second approach for estimating the regional C_6H_6 flux, CH_4 emission rates are taken from the spatially resolved emissions inventory developed for the entire Barnett Shale.[29] Background corrected VOC mixing ratios were used to determine source-specific molar ratios relative to CH_4, as was previously done to estimate regional ethane emissions.[31] Average molar ratios (Table S3) help to lessen biases that arise from sampling only those ONG sites with larger leak rates. These "fat-tail" sites (including well pads, compressors, and processing facilities) contribute roughly 20% of ONG emissions in the region.[29] Overall, the Barnett Shale emits 72,300 kg CH_4 h^{-1}, of which 67% come from thermogenic sources, or 48,400 kg CH_4 h^{-1}. Biogenic sources were not shown to emit significant amounts of heavier alkanes and aromatics, so only the contributions from thermogenic sources are factored into the calculations (Supporting Information). The median emissions estimate is 56 ± 4 kg C_6H_6 h^{-1}. Including low-end and high-end CH_4 estimates (42,100−56,400 kg h^{-1}) gives a range of emissions of 51 ± 4 to 60 ± 4 kg C_6H_6 h^{-1} for the entire Barnett Shale region.

To verify that urban sources (combustion, water treatment plants, landfills) did not overly influence background samples used for mixing ratio corrections, the isopentane to n-pentane ratio was utilized. Previous studies have shown that emissions from vehicular combustion have a higher proportion of isopentane, thus elevating the iso- to n-pentane ratio.[39] For instance, in an urban environment like Pasadena, CA the ratio was 2.41, compared to ONG locations in Colorado such as Wattenberg Field or Erie/Longmont, which had ratios of 0.86 and 0.965, respectively.[40,41] In the Barnett background samples, the iso- to n-pentane ratio was 0.88 ± 0.8 (linear regression, R^2 = 0.83), suggesting that ONG emissions are dominant in the region.

Regional estimates of HAPs derived from both mobile flux measurements and the CH_4 inventory are summarized in Table 4. With the exception of benzene, MFP-derived rates are approximately 1.5−2.5 times larger than inventory-based values. For the m- and p-isomers of xylene, however, the estimates differ by a factor of 6. The cause of this large discrepancy may be a result of where samples were collected. The highest hexane and m/p-xylene mixing ratios observed during this campaign were downwind of well pads with compressors, where mobile CH_4 leak rates were highest. When compared to the Barnett Shale Special Inventory, developed by the TCEQ for the year 2009, the regional inventory-derived values calculated here are higher. HAP emissions for the 23-county Barnett Shale region

Table 4. Comparison of Regional Fluxes (in kg h^{-1}) for Each of the HAPs Measured Including Hexane, Benzene, Toluene, Ethylbenzene, and the Isomers of Xylene, Derived from MFP Measurements and the Barnett Shale Regional Inventory

	CH_4[28]	C_6H_{14}	'B' C_6H_6	'T' C_7H_8	'E' C_8H_{10}	m/p-'X' C_8H_{10}	o-'X' C_8H_{10}
MFP		1070 ± 340	53 ± 17	257 ± 96	16 ± 5	428 ± 167	33 ± 13
inventory							
low	42,100	642 ± 45	51 ± 4	160 ± 11	8.2 ± 0.6	68 ± 5	11 ± 1
median	48,400	687 ± 49	56 ± 4	171 ± 12	9.0 ± 0.6	72 ± 5	12 ± 1
high	56,400	742 ± 53	60 ± 4	186 ± 13	9.4 ± 0.7	78 ± 6	12 ± 1

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totaled 1,080 tons per year (tpy) or 123 kg h^{-1} for all hazardous compounds (n = 200), compared to over 1,000 kg h^{-1} for the 6 compounds measured in this study.[42] A similar result is observed when quantifying total VOC emissions. The TCEQ Special Inventory estimates emission of 20,800 tpy (2400 kg h^{-1}) for C_3+ alkanes, while another study puts this value at 25,300 tpy (2900 kg h^{-1}).[42,43] Calculation of C_3−C_5 alkane emissions using UCI background corrected canister samples approximates emissions equal to 10,300 kg h^{-1}. One possible explanation for the difference is that a higher proportion of episodic, large emissions was captured by samples in the current study, whereas the previous studies, which rely on self-reporting and averaged monitoring site data, may have missed those emission events.

Comparisons to Other Regions and Implications for Human Health. Whole air samples collected in the Barnett Shale reveal a significant regional source of potentially toxic VOCs from oil and natural gas activities. Mean mixing ratios and emission rate estimates of hexane, benzene, and toluene in the Barnett were similar to values witnessed in ONG producing regions of Colorado and Utah.[40,44] For instance, as part of the 2012−13 Winter Ozone Studies campaign, continuous monitoring of VOCs from a tall tower and tethered balloon revealed emissions of 183 kg h^{-1} of benzene and 228 kg h^{-1} of toluene in the Uintah Basin.[44] The basin, located in northeastern Utah, serves as one of the highest producing oil and gas fields in the US and is home to over 4000 oil and 7000 natural gas wells.[44,45] Despite the smaller number of gas wells compared to the Barnett, the Uintah Basin is also home to active coal mines which potentially contribute to the increased benzene and toluene emissions.[46] In another study conducted in the Houston Ship Channel, VOCs were measured from petrochemical facilities and storage tanks. Average emissions rates of benzene were 460 tons per year, or 53 kg h^{-1}, equivalent to emissions determined in the present study.[47]

The findings presented here suggest a significant regional source of hazardous air pollutants in the Barnett Shale. The potential impacts associated with these emissions are 2-fold: the presence of highly reactive non-methane hydrocarbons could lead to increased surface level ozone (particularly of concern in the DFW NAAQS nonattainment region) and human health impacts associated with exposure to such compounds. The extent to which the emission of these HAPs equates to a larger public health risk is still uncertain though, with some signs suggesting ONG emissions are not of concern for acute health risks. For instance, federal standards regulated by OSHA set 8-h workplace exposure limits of 1 ppm for benzene and 200 ppm for toluene.[48] NIOSH recommended exposure limits are more stringent, at 0.1 ppm for benzene and 100 ppm for toluene.[49] Maximum values observed in the Barnett Shale for these gases were well under these standards, at 4.2 and 17.8 ppb, respectively. However, exemptions to the OSHA standards do exist for crude before it is sent downstream for processing. Some of the highest benzene and toluene mixing ratios in this study were upstream near oil wells, suggesting that workers who manually sample these liquids may be at higher health risk.[49] In addition, a recent study using data from TCEQ monitoring sites throughout the Barnett Shale found that VOC concentrations in the region do not exceed many of the state and federal health regulations and standards.[13] However, it should be noted that the majority of data in that study were from monitoring stations in the dry gas region of the Barnett. As the current work shows, areas with wetter natural gas or conventional oil generate more VOC-enriched emissions.

There is also some evidence to suggest that public concerns for potential chronic health risks are not unwarranted. In the Barnett Shale, the TCEQ sets Effects Screening Levels (ESLs) to regulate ambient levels of benzene considered safe. For long-term exposure concerns, the ESL could be as low as 1.4 ppb, which some oil and gas sites sampled in the current study did exceed.[50] Furthermore, previous studies have shown that even low exposure rates of carcinogens can potentially be harmful to a population. Increased incidence rates and risk of cancer have been observed in communities living downwind of industrial facilities, even with VOC emissions that comply with federal standards.[15,51,52] In Colorado, a study examining birth outcomes and proximity to natural gas development between 1996 and 2009 suggested a link between mothers living within 10 miles of active natural gas wells and occurrence of congenital heart defects and neural tube defects in infants.[53] Overall, more than 80% of peer-review articles published between 2009 and 2015 that discuss unconventional ONG development have indicated public health hazards.[54]

Ultimately, it appears that the type of fossil fuel and where it falls in the supply chain play an important role in overall emissions observed downwind. Processed, distribution-grade natural gas is not a significant source of HAPs or hydrocarbons beyond the light alkanes in the Barnett Shale (Tables 1 and 2). This was also observed in the recent Aliso Canyon natural gas blowout near Los Angeles, CA. The massive leak from an underground gas storage facility was the largest anthropogenic CH_4 point source in the nation, lasting nearly four months and emitting up to 60 metric tonnes of CH_4 per hour.[55] However, because the leak was distribution-grade gas, it did not release a significant amount of aromatic compounds (although the health impacts of exposure to odorants such as methyl mercaptan have yet to be quantified). Emission rates calculated from reported molar emissions ratios correspond to 1.5 ± 0.2 kg h^{-1} of C_6H_6 and 2.2 ± 0.3 kg h^{-1} of C_7H_8. These are much lower than emission rates from oil wells, wet natural gas, and compressor stations presented in the current study.

One aspect not explored in this study, unfortunately, was the difference in emissions during the various stages of a well's lifetime. During well drilling or hydraulic fracturing for instance, VOC emissions may be significant, potentially stemming from fugitive emission, combustion exhaust of drilling rigs, or diesel engines.[2,26,56] Two whole air samples collected at fracking sites were slightly enhanced over background for most VOCs measured but not as high as other ONG sources (Table 1). However, sampling conditions were not ideal (low winds, obstruction from construction walls), and these samples are not considered a good source representation. Flowback operations and well completions were also not targeted for sampling but are believed to increase the risk of health impacts for those working near wells or living in close proximity.[14] Despite the limited number and type of ONG sites samples in this work, measurements do suggest an important local source of these toxic compounds and stress the need for continued measurements from both operators and regulators.

In summary, whole air samples collected in the Barnett Shale revealed an enhancement of numerous hydrocarbons from each of the oil and natural gas sources sampled. Among these enhanced VOCs were potentially toxic compounds including hexane and aromatic compounds, which were 2−50 times greater than the local background on average. Emission

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estimates for these gases suggest a significant regional source, concerning to the large population that lives close to the extensive ONG infrastructure. While it does not appear that emissions caused enhancements that exceed federal workplace guidelines for short-term exposure, benzene enhancements exceeding ESLs highlight the need for continued VOC monitoring, as the potential for human health impacts for long-term exposure exists. More research is needed to address uncertainties in emissions and human exposure, particularly as natural gas production from unconventional sources continues to expand on a global scale.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b02827.

Raw data and Tables S1−S3 (XLSX)

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Notes

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